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13. SUPPLEMENTARY NOTES Due to lack of funding, this project was terminated in January 2003. The first year's interim report serves as the Final Report for the project.						
14. ABSTRACT This report results from a contract tasking Ben-Gurion University of the Negev as follows: The Contractor proposes to investigate the possibility of reversibly tuning the conductivity and (linear and nonlinear) optical properties of conjugated chains via protonation. Protons, the smallest chemical species, are generally mobile, and hence offer the potential for reversibility. Equally importantly the concepts proposed herein do not rely on as strongly on redox chemistry, but rather on acid-base chemistry. This may produce species more stable than those produced by addition of powerful oxidizing agents and not be as harmful to the polymer structure. Finally the principles outlined will be used to explore charge pumping and control in these materials. The principal methods to be used: synthesis of conjugated systems, their UV/Vis and NMR analysis under various acid-dopants and conditions, and computational chemistry to support and rationalize the results.						
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Scientific report 3, for the period: July 16, 2002 to November 15, 2002

Due to lack of funding, this project was discontinued in January 2003. This report serves as the final report for the project.

"Reversible Tuning of Optical and Electronic Properties for Component Integration in Molecular and Nano-Electronics"

SPC 01-4083, contract order number F61775-02-WE083

Objectives for this period:

- 1) Continuation of UV/Vis spectroscopic monitoring of acid titration of various imines, in order to assign the protonation site and study its effect on structure and properties.
- 2) NMR (¹H and ¹³C) monitoring of the acid titration of imines, for the same purpose: accurate determination of the protonation site in imines with several nitrogen atoms.
- 3) In collaboration with other scientists (Prof. Khodorkovski of this Department) we have prepared a small amount of a new polyconjugated system containing one nitrogen in the conjugated chain for every five carbons. No tests have as yet been performed, because of the small quantity, but this material is of great promise, and will be tested in the future for conductivity, and the effect of acid doping upon conductivity, as soon as more material becomes available.

Progress:

- 1) Acid titration of imine **1**.

The simplest of imines, cinnamaldehyde-anilineimine (**1**) has been prepared in very pure form, and subjected to the UV/Vis analysis. The resulting UV spectra, representing **1** with an increasing concentration of added trifluoroacetic acid (TFA), are shown in Figure 1.

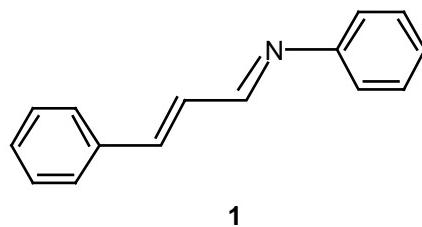
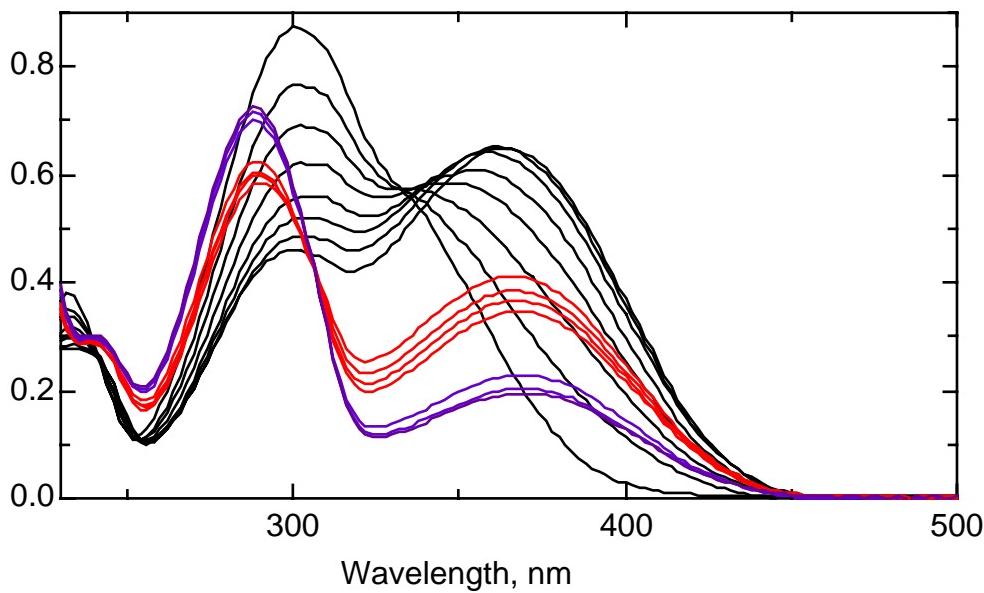


Figure 1 : Titration of imine **1 with TFA in CH_2CL_2**

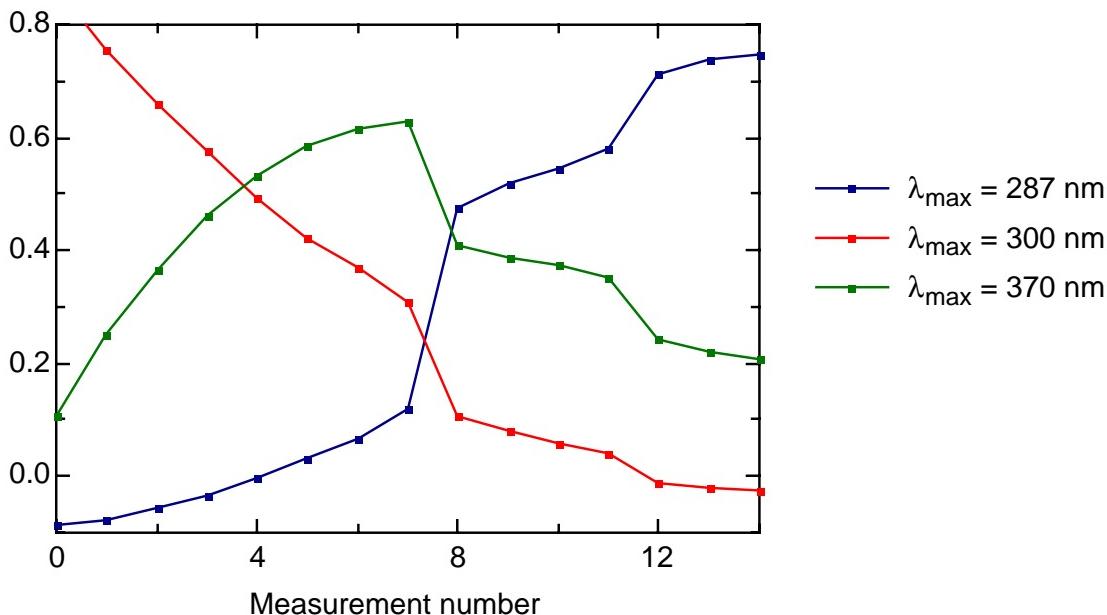


The spectra were run at short intervals using an air-tight UV cell and adding the TFA solution in 1 μL portions from a microsyringe. The spectra are grouped in three color-coded series, black, red and violet. The first eight spectra (black) were run at short intervals, after which a 15-minute break was taken followed by a second run of *the same sample*, without addition of acid. The same procedure was repeated for the four spectra coded red, followed, after another 15-minute break, by the violet-coded spectra. The dramatic spectral changes which are evident from Figure 1, resulting *only* from the 15-minute wait periods, (the changes separating the three color groups) led to the conclusion that substantial hydrolysis of the imine took place during the UV measurements, independently of the addition of acid. The high moisture sensitivity is enhanced by the fact that very low concentrations are used for UV measurements, and thus any residual solvent-moisture or humid air may cause substantial decomposition. This result is in agreement with the difficulty to obtain very pure and water-free **1**, due to its rapid hydrolysis.

The UV measurements were analyzed, as described in the previous report, by fitting the spectral lines to three Gaussian components, centered at 287, 300 and 370 nm wavelengths (Figure 2). Indeed, the relatively rapid decomposition of the imine is immediately recognized from Figure 2: there are two sudden and irregular changes in all three lines. These changes represent the time intervals, which allowed decomposition of the mixture of components. Despite the decomposition, the general trend is reasonable: the starting material **1** (red line) is consumed by the addition of acid, resulting in a homogeneous decrease in its absorbance and concentration. There is an initial buildup of a protonated species (Green), which rapidly decomposes upon standing and converts to the hydrolysis product (Blue). The distinct consumption of the protonated intermediate and formation of the decomposition product, indicate

that this particular imine is not sufficiently stable for the acid doping, and hence is an inadequate model for the charge distribution in partly-protonated imines.

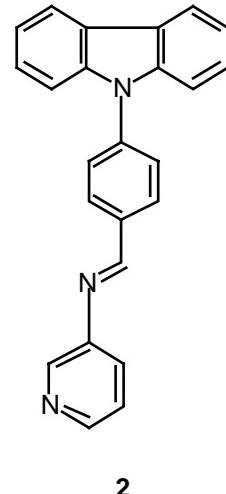
Figure 2: Titration of imine **1** with TFA in CH_2Cl_2 ; evolution of 3 components



2) Acid titration of imine **2**.

Imine **2** is a solid and stable imine, which does not hydrolyze significantly under normal conditions. Its synthesis was reported in the previous report.

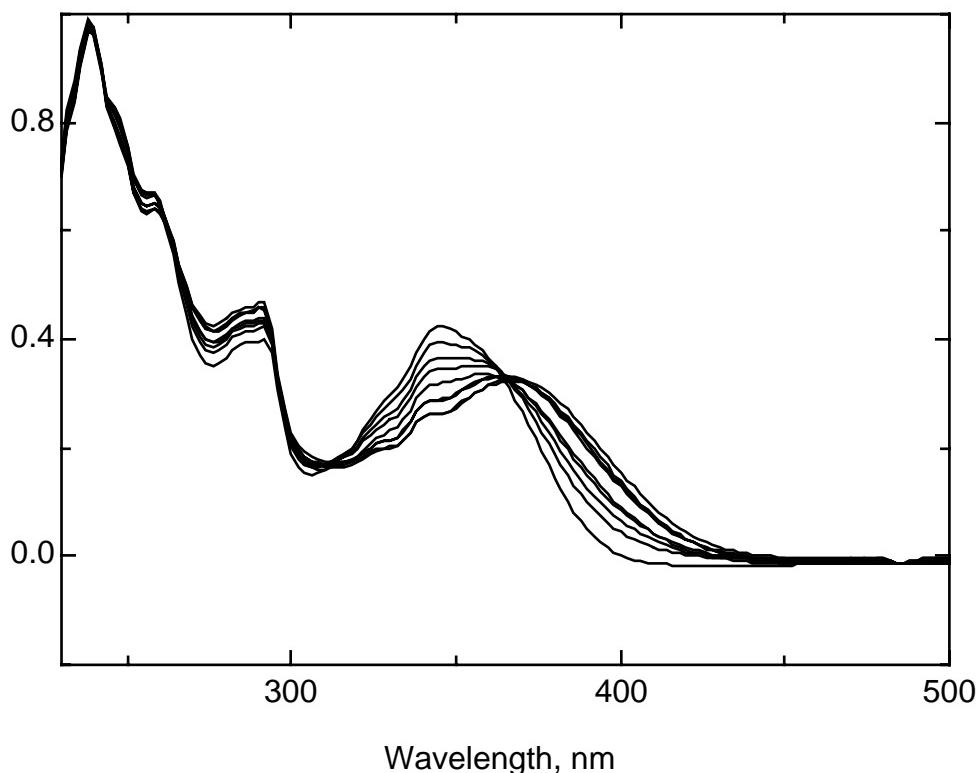
Application of the UV/Vis titration method, as applied and described for **1** and in previous reports, led to the series of UV spectra depicted in Figure 3. In contrast to the UV analyses for **1** and those described in the previous report, in which several components were involved and decomposition was observed during the analysis, in this imine (**2**) protonation did not result in significant decomposition. This is evident from the sharp isosbestic point found at $\lambda = 328 \text{ nm}$: the fact that all of the spectra have *one* common point at a given wavelength is evidence of a *two-component* system, i.e., during the time frame of the measurements only the starting imine and the protonated product are present, with no significant amounts of other species.



Despite the expected simplicity of a two-component system, it has been impossible so far to use the gaussian-fit procedure (used successfully for other imines) for a quantitative component analysis. This is because of the complexity of the spectra, and the severe deviations from symmetrical gaussian shapes of the UV absorptions, as apparent in Figure 3. Attempts at a number of components, up to 8 gaussian

contributions, did not yield satisfactory spectral simulations and were hence rejected. However, the gradual decay of the absorption at $\lambda_{\max} = 343$ nm, and the parallel evolution of an absorption at $\lambda_{\max} = 380$ nm, is in complete agreement with previously studied imines in which the protonated-imine absorption maximum was shifted about 40 nm to longer wavelength relative to the parent imine.

Figure 3 : Titration of imine **2 with TFA in CH_2Cl_2**



Despite the clean spectral analysis showing disappearance of starting material **2** and evolution of a single protonated product, the available UV information does not allow assignment of the protonation site to one of the three nitrogen atoms in **2**. As a result, we had to resort to NMR spectroscopy for a more accurate analysis.

3) NMR analysis of the protonation of **2**.

A complete assignment of the ^1H and ^{13}C NMR spectra of **2** in CDCl_3 solution has been accomplished with the aid of a ^1H - ^{13}C 2D-NMR correlation spectrum shown in Figure 4. The carbon (and corresponding proton) labels are shown next to Figure 4. The assignment was also verified by a calculation using the CHEM-3D program. In Figure 4, quaternary carbons, which have no proton counterpart or cross peak in the 2D spectrum, are labeled on the carbon-projection spectrum.

Figure 4: H1-C13 NMR Correlation Spectrum for **2**

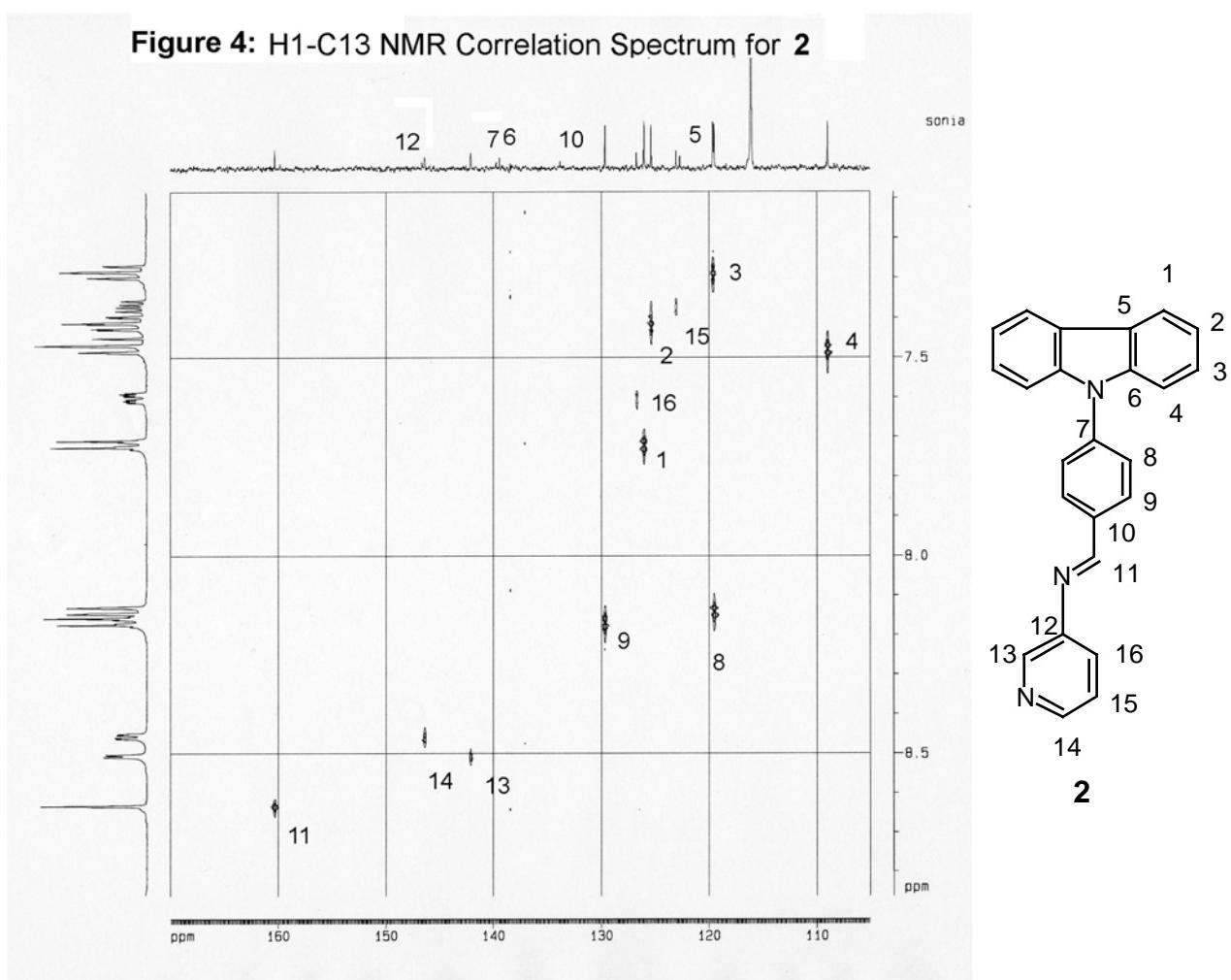
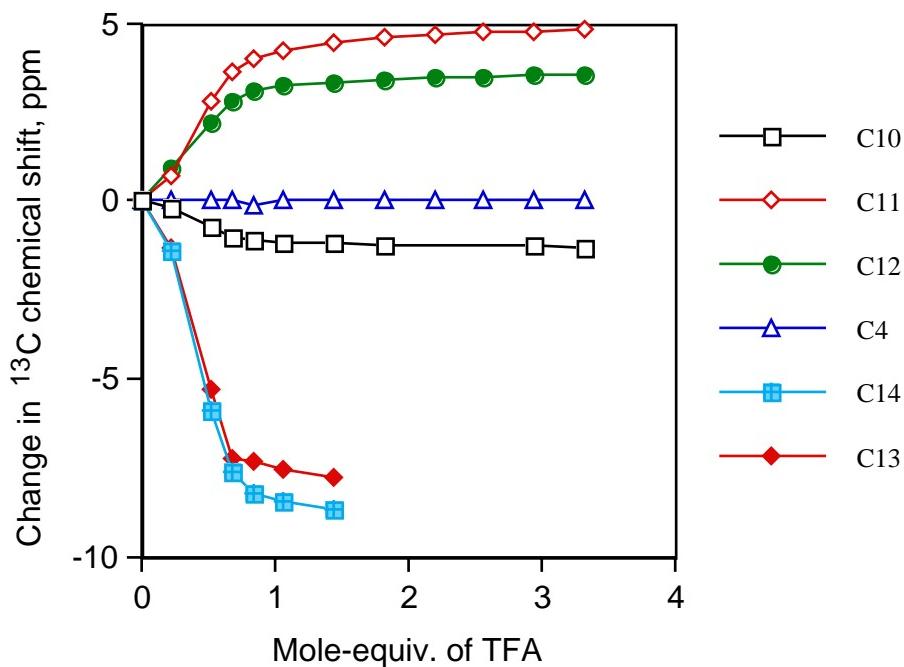


Figure 5: Change in ^{13}C Chemical Shift for **2** vs. Added TFA



The changes in the ^1H and ^{13}C NMR spectra resulting from the acid (TFA) titration of **2** in a 1:1 mixture of CDCl_3 and CD_3CN was studied, and the results for selected carbons of **2** are presented in Figure 5.

This method is found by far superior for this analysis than the UV/Vis method, for several reasons: (a) because of the rather substantial concentrations of solute in NMR samples, the sensitivity to residual unavoidable moisture is not as critical as in UV measurements. (b) The analysis of the effect of added acid on *individual* carbon atoms in the molecule allows a much better understanding of the protonation site and possible charge distribution.

The data in Figure 5 show dramatic changes in the NMR spectra resulting from protonation. It is also evident from the Figure that the major changes take place as a result of the addition of one mole-equivalent of TFA, i.e., the molecule probably undergoes a single protonation process, even in presence of excess acid. The chemical shifts of the carbon atoms belonging to the carbazole system (C1 – C6) are only marginally affected by the addition of acid. This excludes the carbazole nitrogen as a possible protonation site. Carbons 13 and 14 are the ones most strongly perturbed by added TFA. This strongly suggests that protonation takes place at the pyridine-nitrogen flanked by C13 and C14. However, the change in chemical shifts for these two carbons is to *higher* field, in contrast to intuitive expectation. This direction of change may be associated with a decrease in the aromatic ring current, as a result of protonation.

Protonation of the imine-nitrogen can also be ruled out, based on the minimal changes in chemical shifts found for the central-ring carbons: C7 - C10. If protonation had taken place on the imine-nitrogen, one would have expected a substantial contribution of the canonical structure depicted in **3**, a quinoid species. Involvement of **3** should have caused significant changes in the chemical shifts of C1 - C10, which are not observed.

These experiments suggest that protonation does take place on nitrogens in the conjugated chain of imines, and that a polymer based on a conjugated system of carbons and some nitrogens may be protonated by one-half of a mole of acid, to produce an effective conduction band. The next step in the project should be experimentation with such potential conductors.

4) The $[(CH_2)_5N]_n$ oligomer and polymer.

In collaboration with other scientists, we have received a small amount of a polymer with the suggested structure shown above. The amount of material has been too small to permit any serious manipulation. We are waiting for a second batch of this material (the preparation of which has not yet been disclosed) in order to directly test its conductivity, and how it is affected by acid doping.